A STUDY ON THE EFFECT OF VARIOUS ELECTROLYTIC PARAMETERS ON THE PERFORMANCE OF METAL OXIDE THIN FILMS FOR PHOTOELECTROCHEMICAL SPLITTING OF WATER

A synopsis of the proposed work for the award of the degree
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in Chemistry

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1. Introduction

1.1 Energy scenario

Energy is the major input for economic development of every country. Most part of energy currently is supplied by fossil fuel in the world & it is estimated that world consumption of primary energy (coal, oil, natural gas and biomass) is approximately 9741.1 million tonne oil equivalent. India is 7th major primary energy consumer in world and consumes approximately 345.3 million tonne oil equivalent[1]. Major energy sources (renewable energy and non-renewable energy sources) are shown in Figure 1.

It is estimated that the distribution of global energy is about 80% fossil, 14% renewal energy, 6% nuclear power[2]. Share of renewable energy sources is expected to increase very significantly (30–80% in 2100)[3]. At present, consumption of fossil fuels is a major cause of air pollution. SO_2, NO_x, CO, O_3, hydrocarbon, benzene etc. are responsible for climate change, acid rain and greenhouse effect. Air pollution has both chronic and acute effect on humans and cause diseases such as lung cancer, acute respiratory infection in children and chronic bronchitis in adults.

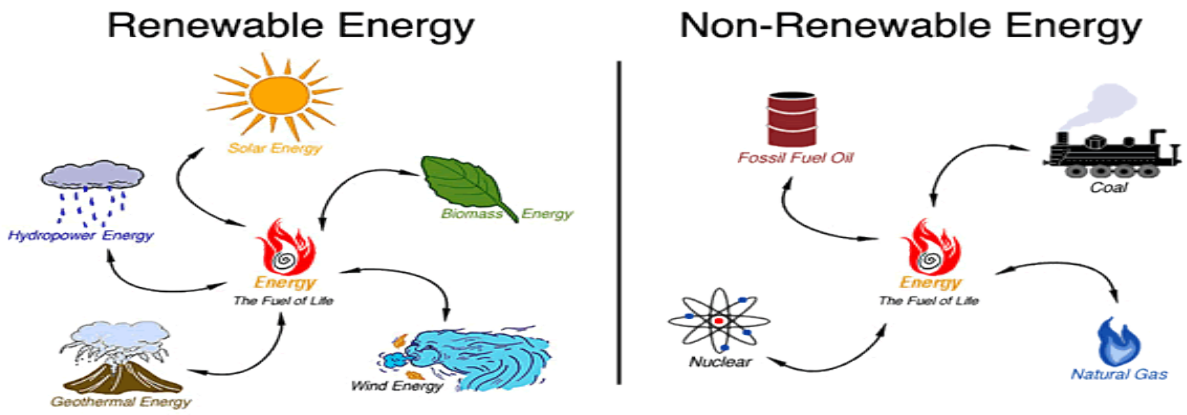

Figure 1- Renewable energy and non-renewable energy sources[4]

Renewable energy sources are considered as clean sources of energy. The optimal use of renewable resources would minimize environmental impacts and produce minimum secondary wastes. Renewable energy sources are geothermal, biomass, solar, hydropower, wind and marine energies. Heat and light is primary forms of solar energy. Sunlight and heat are transformed and absorbed by

the environment in a multitude of ways. Some parts of these transformations result in renewable energy flows such as biomass and wind energy[5-6]. At large-scale, hydropower supplies 20% of global electricity[7]. Wind power in coastal and other windy regions is a promising source of energy[3,8].

1.2 Solar Hydrogen: A sustainable energy carrier

Hydrogen is known as fuel for future. Hydrogen generated from water using solar energy is a leading candidate for a renewable and environmentally safe energy carrier due to the following reasons[9] : (i) solar-hydrogen technology is relatively simple and, therefore, the cost of such a fuel is expected to be substantially less than that of the present price of gasoline, (ii) the only raw material for the production of solar-hydrogen is water, which is a renewable resource and (iii) large areas of the globe have ready access to solar energy which is the only required energy source for solar-hydrogen generation.

The solar hydrogen fuels will be able to reduce our dependence on natural gas and oil in the world. There is a growing awareness that hydrogen energy may help avoid the next potential energy crisis, which will be driven by an increasing dependence on the existing sources of energy[10]. Already, there are prototype hydrogen-powered cars and buses on the road. It is only a matter of time before gasoline stations begin to adapt their infrastructure to hydrogen distribution. It is possible that, within ~15 years, if most of the gasoline stations will be converted to hydrogen stations[11].

In the quest for new energy sources, hydrogen stands out as an attractive alternative energy carrier on account of various properties. It has high heat of combustion (34.18 kcal/g for H_2 and 10.30 kcal/g for petroleum) and energy released by hydrogen is 140 kJ/g while methane releases only 33 kJ/g. It produces water upon combustion so that emission of greenhouse gases will be negligible. Energy storage capacity/mole of H_2 is 119 kJ/g while that of oil is 40 kJ/g. It can be stored in gaseous, liquid or metal hydride forms and can be transported over large distances through pipelines or via tankers and can be converted into other forms of energy in more efficient ways than any other fuel[12].

1.3 Photoelectrochemical cell

Many techniques are used to generate hydrogen gas. They are principally divided into 5 groups : (a) Water Electrolysis, (b) Process applying ionizing radiation (homogenous nuclear reactor, chemonuclear reactor, fusion process), (c) Thermochemical system (open and closed) (d) Biological system (in vivo e.g. prokaryotic bacteria etc; in vitro: using biological components) and (e) Photochemical, photoelectrochemical and photovoltaic-electrolysis system using solar energy[12]. Photoelectrochemical (PEC) technology is the most promising technology for hydrogen production by water splitting. PEC technology is based on solar energy and water, both of which are abundantly available and it is totally safe for environmental, with no undesirable by products. PEC technology is relatively uncomplicated and may be used on both large and small scales.

The performance of photoelectrochemical cell is considered in terms of excitation of electron–hole pair in photo-electrodes, charge separation in photo-electrodes, electrode processes and related charge transfer within PECs and generation of the PEC voltage required for water decomposition. The general arrangement of PEC cell involves[13]: (i) Photo-anode made of n-type semiconductor and cathode made of metal; (ii) Photo-anode made of n-type semiconductor and photo-cathode made of p-type semiconductor; (iii) Photo-cathode made of p-type semiconductor and anode made of metal. Schematic diagram of photoelectrochemical cell is shown in Figure 2.

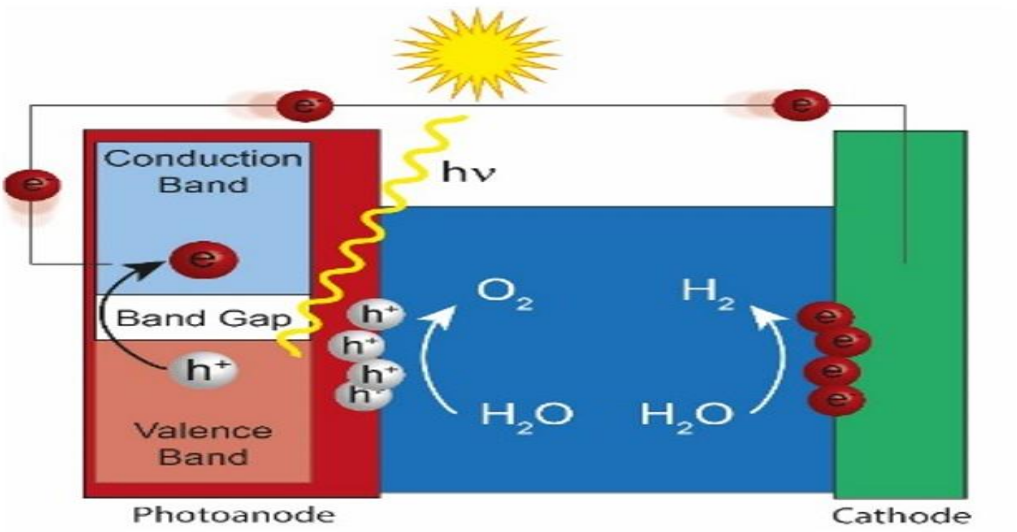

Figure 2- Photoelectrochemical cell[14].

In the PEC water-splitting process, oxygen (O_2) evolution at the anode and hydrogen (H_2) evolution at the cathode can be modeled as two electrochemical "half-reactions." A simplified set of equations describing the half-reactions in addition to the net conversion process can be written as[15]:

2γ	$\rightarrow 2\,e^- + 2\,h^+$	Photon-induced electron-hole pair generation
$H_2O + 2h^+$	$\rightarrow 2\,H^+ + \frac{1}{2}\,O_2$	OER : anodic water-oxidation half-reaction
$2H^+ + 2e^-$	$\rightarrow H_2$	HER : cathodic H^+ reduction half-reaction
$H_2 + 2\,\gamma$	$\rightarrow H_2$ (gas) $+ \frac{1}{2}\,O_2$ (gas)	Net PEC water splitting reaction

In photoelectrochemical cell, an ideal photo anode should have following features: (a) band gap 1.6-2.0 eV, (b) durability>2000hr, (b) be corrosion resistant, (c) be stable in electrolytes, (d) maximum absorption of sunlight at surface, (e) be inexpensive and (f) be easy available. High band gap materials are poor harvesters of solar radiations and do absorb in the UV region of light, but exhibit high stability in aqueous electrolytes. e.g.- TiO_2 (3.2 eV), WO_3 (2.6 eV), $SrTiO_3$ (3.3 eV), $BaTiO_3$ (3.3 eV), SnO_2 (3.8), ZnO (3.2 eV). Low band gap Materials are good harvesters of solar radiations but exhibit poor stability in aqueous electrolyte. e.g.- Si (1.14 ev), GaAs (1.4 ev), InP (1.42 ev), CdTe (1.61 ev), CdSe (1.7 ev), CuO (1.2 ev). Researchers are involved in developing the ideal semiconductor with the above said properties but so far the success has eluded them and the search for an ideal semiconductor is far from over. Figure 3 shows band position of some semiconductor materials and relative energies with respect in terms of vacuum level and normal hydrogen electrode level (NHE) in electrolyte of pH = 1.

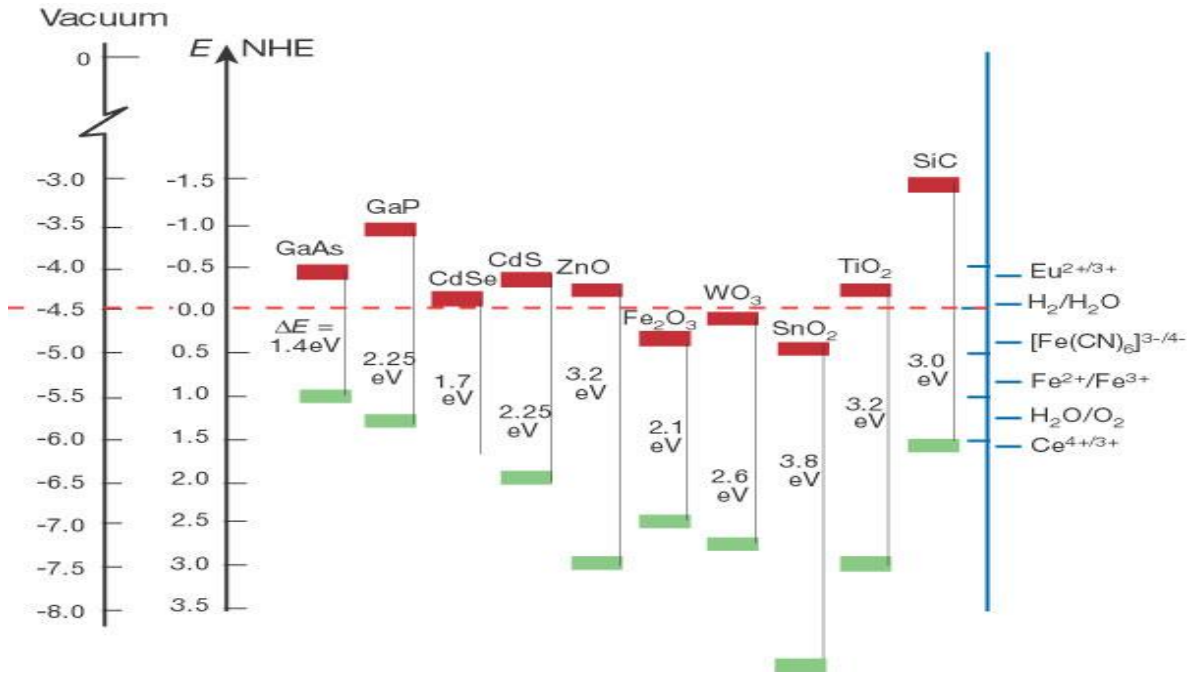

Figure 3 Band position of several semiconductor materials in electrolyte of pH = 1[16].

1.4 Effect of electrolytic parameters on PEC splitting of water

Electrolytic parameters, like temperature, pH, ionic strength etc, affects the performance of photoelectrochemical cell.

Effect of temperature

Photoelectrochemical cells are very sensitive to temperature. With increase in temperature, energy band gap of a semiconductor reduces and the generated photocurrent density increases due to lower energy photons are also absorbed. The dependence of the band gap energy with temperature (T) is given by the Varshni model as shown in equation (1).

$$E_g(T) = E_g(0) - \frac{\alpha' T^2}{T + \beta'} \quad \text{..... (1)}$$

$E_g(T)$ is band gap of the semiconductor at 0 K, α' is the limit of gap energy when $T \rightarrow \infty$, β' is expected to be comparable with the Debye temperature θ_D for a given material[17-18].

Effect of pH

The pH of electrolytes affects the performance of photoelectrochemical cell. Stability of semiconductor also depends upon pH of electrolytes. TiO_2 nanoparticles are usually soluble in highly basic (pH above 10) aqueous solutions. Photocurrent density also get affected at different pH. The pH of electrolytes significantly influence the rate of hydrogen production and quantum yield (QY) for water splitting in solar cell[19].

Effect of Ionic Strength

Ionic strength of electrolytes affects the performance of photoelectrochemical cells. Ionic strength effects the output of PEC cell by ionic mobility, charge transfer, stability of electrodes.

The ionic strength (I) can be represented by equation (2)[20].

$$I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \qquad \text{..... (2).}$$

Where c_i is the molar concentration of ion and z_i is the charge number of ion i. In regard to effect of electrolytic parameters (like temperature, pH, ionic strength etc.) in the performance of PEC cell, little work has been done. Comprehensive and comparative study on these aspects are missing. It is therefore needed to study the performance of photoelectrochemical cell with reference to electrolytic parameters as detailed above in a systematic manner.

1.5 Metal Oxides

Semiconductor materials like TiO_2 and Fe_2O_3 are material of interest in the present study and brief details of these materials are given below.

Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) is considered as an ideal semiconductor for photoelectrochemical cell because of its low cost, high stability and safety toward both environment and human. It is found in orthorhombic and tetragonal phase. Titanium dioxide (TiO_2) can be synthesized by different ways, like Sol gel method**,** Spray pyrolysis method and Electrodeposition method.

Titanium dioxide (TiO_2) has band gap of approximately 3.2 eV which comes under the category of large band gap material. Fe, Cd and Sn doped Titanium dioxide (TiO_2) exhibited significantly improved photocurrent density[21-23].

Hematite (Fe_2O_3)

Compared to other semiconductors, hematite (Fe_2O_3) has many potential advantages for hydrogen production in PEC devices. It is an n-type semiconductor that is stable in most electrolytes at pH > 3 and has a narrow band gap, 2-2.2 eV, sufficient to utilize approximately 40% of the incident sunlight. Fe_2O_3 thin film can be prepared by different ways like Sol gel method**,** Spray pyrolysis method and Electrodeposition method[24].

It has been reported that an optimal band gap of 2.46 eV[25] is required for water photo-oxidation without external bias. Band-gap of hematite reported to be around 1.9-2.2 eV (depending on its crystalline status and method of preparation)[26]. A large number of dopant species have been introduced into Fe_2O_3 attempting to improve photoelelectrochemical performance including Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Si^{4+}, Ge^{4+}, Ti^{4+}, Pt^{4+}, V^{5+}, and Nb^{5+} [27]. Zn-Dotted Hematite thin films exhibited significant photocurrent density[28]. Electrodeposited zirconium-doped α-Fe_2O_3 thin film shows enhanced photocurrent density[29].

2. Literature survey

The summary of work done in the area of photoelectrochemical water splitting in the recent years is described below presenting different methods of synthesis, characterizations and PEC response of various metal oxide materials.

- Patil[30] et al, (1989) prepared n-Fe_2O_3 thin film on FTO coated glass substrate by pyrolytic decomposition and studied the effect of temperature on the performance of the cell. They observed that flat band potential shifted in the anodic direction with increasing temperature and decay time decreases with increasing temperature.

- Wang[31] et al, (2006) synthesized Single-phase multiferroic $BiFeO_3$ thin films on 111 Pt/Ti/SiO_2/Si substrates via a simple sol-gel spin-coating technique, as evidenced by X-ray diffraction. The thickness of the films can be controlled by the number of layers spin coated. Scanning electron microscope confirmed good surface and cross-section morphology of the films. X-ray photoelectron spectroscopy was used to examine the combination state of Fe 2*p* electron in the $BiFeO_3$ films.

- Wang[32] et al, (2007) studied the effects of pH photoelectrochemical properties of TiO_2 photoelectrode and observed that short circuit photocurrent and open circuit voltage of TiO_2 photoelectrode increased as solution pH decreased.

- Joshi[33] et al, (2008) synthesized single-crystalline perovskite nanocubes composed of bismuth ferrite $BiFeO_3$ sizes ranging from 50 to 200 nm by a simple microwave procedure. The single-crystalline nature of nanocubes was confirmed by high resolution transmission electron microscopy and selected area electron diffraction pattern. X-ray diffraction pattern showed the rhombohedral phase with *R*3*c* space group. The material showed photoinduced water oxidation activity in both photoelectrochemical and photocatalytic modes.

- Zhang[34] et al, (2009) synthesized BiOI/TiO_2 heterostructures characterized by XRD, nitrogen sorption, electron microscopy, UV−Vis diffuse reflectance spectroscopy, X-ray photoelectron

spectroscopy and surface photovoltage spectroscopy. They observed that BiOI/TiO_2 heterostructures exhibited much higher photocatalytic activities than pure BiOI and TiO_2, respectively. 50% BiOI/TiO_2 heterostructure showed the best activity.

- Zhang[35] et al, (2010) studied effects of electrolyte pH and photo-catalyst on onset potential of photoelectrochemical cell. They observed that Silicon, SiC and Micromorph cells showed a changing response with pH, as expected from the relationship between doping and acidity.

- Cho[36] et al, (2011) synthesized branched TiO_2 nanorod on FTO and characterized by SEM, TEM, HRTEM. The branched Titanium oxide (TiO_2) nanorod array produced a photocurrent density of 0.83 mA/cm^2 at 0.8 V vs RHE.

- Kim[37] et al, (2011) synthesized ZnO/WOx heterostructures that exhibited enhanced photoelectrochemical properties when used as photoanodes. ZnO/WOx heterostructures produced a high photocurrent density of 11mA/cm^2 at -0.5V vs SCE for hydrogen generation.

- Wang[38] et al, (2011) prepared Hydrogen-treated rutile TiO_2 (H:TiO_2) nanowires by annealing the pristine TiO_2 nanowires in hydrogen atmosphere at various temperatures. In comparison to pristine titanium oxide (TiO_2) nanowires, H:TiO_2 shows enhanced photocurrent photoelectrochemical water splitting .

- Sharma[39] et al, (2012) synthesized Fe–TiO_2/Zn–Fe_2O_3 thin films characterized by XRD, Raman, AFM, UV-Vis absorption spectroscopy. Heterojunction generate nine times better photocurrent density than pure Fe–TiO_2 and exhibit solar to hydrogen conversion efficiency of 0.77%.

- Zhang[40] et al, (2012) studied photo-voltage of different materials in different pH value Na_2SO_4 solution. They concluded that n-type material prefer alkaline ambient and the p-type material prefer an acidic environment enhanced photo-voltage.

- Abdallah[41] et al, (2013) investigated the effect of pH on the H_2 and O_2 production using photovoltaic power generation system. Water splitting process into H_2 and O_2 occurs when a DC

current generated by a photovoltaic system. Alkaline region gave compatibly better hydrogen production.

- Jiao[42] et al, (2013) demonstrated the fabrication of visible-light-responsive heterostructured Cr-doped $SrTiO_3/TiO_2$ nanotube arrays by a simple hydrothermal method, which facilitate efficient charge separation and thus improve the photoelectrochemical as well as photocatalytic performances.

- Joshi[43], (2013) synthesized single crystal of $MoTe_2$ grown by chemical vapour transport technique used for photoelectrochemical solar cells and observed that efficiency, open circuit voltage and short circuit current of photoelectrochemical cell is dependent upon operating temperature of cell. Open circuit voltages showed a decreasing trend values with increase in the temperature.

- Liu[44] et al, (2013) p-MoS_2/ n-CdS heterojunction films prepared by electrodeposition and chemical bath deposition method and characterized by X-ray diffraction, scanning electron microscopy, UV−visible absorption, X-ray photoemission spectroscopy, photoluminescence, and photoelectrochemical response. Heterojunction exhibitd the highest photocurrent 28 mA/cm^2 and the highest IPCE of ca. 28% at 420 nm at 0 V vs Ag/AgCl.

- Quiñonez[45] et al, (2013) synthesized of high-purity $BiFeO_3$ by a combustion reaction, and characterized through XRD, SEM and HRTEM, TGA, UV−Visible electronic absorption, Raman scattering, Mössbauer, EPR spectroscopies and VSM. The average sizes of the crystallites for $BiFeO_3$ were 26 and 23 nm, for tartaric acid and glycine promoters, respectively. Two band gap energies, 2.27 and 1.66 eV, were found for $BiFeO_3$ synthesized with tartaric acid, obtained from Tauc's plots.

- Ren[46] et al, (2013) investigated photoelectrochemical responses of a TiO_2 nanotube anode in ethylene glycol, glycerol, ethanol, urea, ammonia, and Na_2S electrolytes with different concentrations. They observed that concentration of Na_2S was affected to photocurrent density

and Urea showed high open circuit voltage at proper concentration and low photocurrent at different concentrations.

- Zhang[19] et al, (2013) studied the impact of initial solution pH on hydrogen production using an $Ru/(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ photocatalyst under visible light irradiation. They observed that initial pH significantly influenced quantum yield and the rate of hydrogen production. At pH 2, highest quantum yield (~12.8%) at 420±5 nm and highest hydrogen production rate (~525 μmol h^{-1}) are observed. As increasing pH, the hydrogen production and quantum yield are decreased.

- Dias[47] et al, (2014) studied influence of temperature on the performance of a photoelectrochemical cell prepared with Si doped hematite photoanode and characterized by electrochemical impedance spectroscopy and photocurrent-voltage characteristic curves at different cell operating temperatures. They observed that generated photocurrent density increased with temperature and photoelectrode became unstable above 50^0 C and that the optimal operation temperature of the PEC cell is 45^0 C.

- Hernandez[48] et al, (2014) deposited $ZnO@TiO_2$ core−shells on FTO by sol-gel method. $ZnO@TiO_2$ core−shells heterostructure exhibited photocurrent density 0.40 mA/cm^2 at 1.23 V versus reversible hydrogen electrode (RHE).

- Jiao[49] et al, (2014) fabricated heterostructured TiO_2 nanotube /Cr-doped $SrTiO_3$ nanocubes by hydrothermal reactions and found that coupling TiO_2 nanotube arrays with regular $SrTiO_3$ nanocubes can significantly improve the charge separation. As a result, the rate of photoelectrochemical hydrogen evolution of TiO_2 nanotube/Cr-doped $SrTiO_3$ nanocubes heteronanostructures is an order of magnitude larger than previously reported $SrTiO_3/TiO_2$ nanocomposites under visible light irradiation.

- Li[50] et al, (2014) prepared Cu_2O/ZnO heterojunction by facile two steps of electrodeposition and characterized by scanning electron microscopy, X-ray diffractometry, and UV-Visible spectrophotometer and applied in photoelectrochemical biosensing first time. Using glutathione

as a model, the fabricated photoelectrochemical sensor showed good performances with a rapid response, facile preparation, wide concentration range, excellent stability and low detection limit.

- Minggu[51] et al, (2014) synthesized n-WO_3/p-Cu_2O photoelectrode films on FTO by consecutive electrodeposition of n-WO_3 and p-Cu_2O films from acidic aqueous solution of peroxytungstate and basic aqueous solution of copper sulfate-lactic acid by electrodeposition method. Photocurrent generated by n-WO_3/p-Cu_2O photoelectrode was much higher compared to the plain n-WO_3 and p-Cu_2O.

- Sharma[52] et al, (2014) prepared Fe_2O_3/Cu_2O film by spray pyrolysis method and characterized by XRD, AFM and UV–Vis spectrometry. Heterojunction exhibited significantly higher photocurrent 0.32 $mAcm^{-2}$ at 0.8 V/SCE.

- Sharma[53] et al, (2014) prepared nanostructured thin film Cu_2O/$SrTiO_3$heterojunction and characterized by XRD, SEM, and UV-Visible spectroscopy. Photocurrent density of hetrojunction was 2.52 $mAcm^{-2}$ at 0.8 V/SCE at 343nm overall thickness of heterojunction.

- Wu[54] et al, (2014) synthesized ZnO/Au heterostructure with plasmonic enhanced photoelectrochemical activity for solar hydrogen production. The photocurrent density of the ZnO/Au heterostructure reaches 9.11 $mAcm^{-2}$ at 1.0 V (vs Ag/AgCl), that is higher than pristine ZnO nanorod array (0.33 $mAcm^{-2}$). The solar-to-hydrogen conversion efficiency of ZnO/Au heterostructure can reach 16 times higher than pristine ZnO nanorod array.

- Zhang[55] et al, (2014) synthesized MoS_2/TiO_2/Si coaxial nanowire heterostructure and characterized by HRTEM, XPS, Raman spectroscopy. This heterojunction showed photocurrent density up to 15 mA/cm^2 at 0 V vs. RHE with good stability under operating conditions.

- Zhao[56] et al, (2014) prepared a p-type semiconductor Cu_2O decorated with MoS_2 efficient solar hydrogen production under visible light and characterized by XRD, SEM, TEM and HRTEM. Cu_2O decorated with MoS_2 showed maximum reduction photocurrent density of 0.17mA cm^{-2}vs SCE.

- Zheng[57] et al, (2014) synthesized a 3D hierarchical heterostructure, consisting of cadmium sulphide (CdS) sensitized 1D ZnO nanorods/2D-TiO_2 nanosheet, via a solution process method. This heterostructure show enhanced photocatalytic and photoelectric hydrogen evolution performance compared with CdS sensitized 1D ZnO nanorods/1D TiO_2 nanorods photoanode, as a result of the more efficient light harvesting over the entire visible light spectrum and the effective electron transport.

- Sharma[58] et al, (2015) synthesized Ti-Fe_2O_3/Cu_2O heterojunction and characterized by XRD, scanning electron microscopy, atomic force microscopy, and UV-Vis spectrometry. Ti-Fe_2O_3/Cu_2O heterojunction showed higher photocurrent density and enhanced incident photon-to-electron conversion efficiency. This thin film may be attributed to improved conductivity and efficient separation of the photogenerated charge carriers.

- Urbain[59] et al, (2015) described effect of the operation temperature on the performance of a photovoltaic-biased electrosynthetic cell for solar hydrogen production based on a triple junction thin film silicon solar cell. They studied influence of the temperature in the range from 25 °C - 60 °C. They observed that photovoltage of the solar cells decreased with increasing temperature.

- Dias[60] et al, (2016) deposited WO_3 on a FTO glass and on a tungsten foil in PEC cell and measured electrochemical impedance spectroscopy and Current–voltage curves to characterize these samples between 25 ^{0}C - 65 ^{0}C. They observed that photocurrent density increased with temperature and the optimal operating temperatures observed were 45 ^{0}C and 55 ^{0}C for both the samples.

- Kim[61] et al, (2016) prepared $BiVO_4$ in a 0.1 M KOH solution and found that $BiVO_4$-based photoanodes was more stable and efficient in basic media. They also synthesized $BiVO_4$/$ZnFe_2O_4$ heterojunction and > 2 mA/cm^2 at 1.23 V versus RHE photocurrent density is measured.

- Kwon[62] et al, (2016) synthesized nano-scale n-MoS_2/p-Si heterojunction thin film by CVD method and characterized by AFM, XPS, Raman spectroscopy, UV-Visible spectroscopy. Heterojunction showed high photocurrent density 24.6 $mAcm^{-2}$ at 0 V vs RHE.

- Verma[63] et al, (2016) fabricated Zr-doped Fe_2O_3 sandwiched between two Au plasmonic layer and characterized by XRD, SEM, EDAX and UV-Visible spectroscopy. This arrangement of plasmonic layer showed significant increase in photocurrent density at 0.8 V/SCE.

3. Existing gap in knowledge

Photoelectrochemical performance in the PEC cell is influenced by electrolytic parameters. Electrolytic parameters like pH, temperature, ionic strength affect the photocurrent and efficiency of water splitting by sunlight. Temperature is important parameter because photocurrent of PEC cell increases with the temperature of electrolytes. The band gap of semiconductor changes with temperature which could be optimised for potential water splitting[18]. Temperature may control electrode kinetics, photoelectrode quantum efficiency and electrode stability which in turn may affect the photoelectrochemical performance[64]. Photocurrent depends on the pH of electrolyte and it is due to the reason that pH influence the electrode stability, band edges position of photoelectrode, surface function of electrolytes and ionic mobility[65-66]. Ionic strength is another variable that may influence PEC photocurrent. The effect may arise due to the dependency of ionic mobility, charge transfer and surface function of electrolytes with ionic strength. Generally comprehensive and exhaustive study on these aspects is missing. Work on these aspects will be helpful to add to the knowledge and to produce maximum photocurrent by photoelectrochemical cell at suitable electrolytic parameters (like pH, temperature and ionic strength).

4. Proposed study- An outline

- Preparation of nanostructured thin films of metal oxides (TiO_2, Fe_2O_3) by Sol gel and Spray pyrolysis
- Characterization of thin films of metal oxide nanoparticles by : (i) XRD- To observe the formation of different phases and to estimate the average grain/ particle size using Scherrer's calculations; (ii) SEM and AFM- To observe the surface morphology and topology of the films; and (iii) UV- Visible Spectroscopy: To find the band-gap of the material.
- Photoelectrochemical study of nanostructured thin films by varying electrolytes (KOH, NaOH, Na_2SO_4, K_2SO_4) and other electrolytic parameters such as: pH (9, 10, 11, 12 and 13), temperature (25 ^{0}C, 35 ^{0}C, 45 ^{0}C, 55 ^{0}C, 65 ^{0}C and 75 ^{0}C), and ionic strength (0.10 M, 0.40 M, 1.6 M, 3.1 M, 4.60 M and 6.10 M).

5. Proposed work plan

5.1 Preparation of samples and characterization

Nanostructured thin films will be grown by sol-gel method, spray pyrolysis and electrodeposition method. These methods have already been standardized. Thin films of semiconductor materials would be developed on ITO (Sn doped indium oxide).

Structure and surface morphology

Structural analysis of the samples would be performed by X-ray diffraction technique to check the polycrystallinity of the compound formed and to confirm the formation of desired phase. For determining surface morphologies, such as, grain size (particle size), grain structure and surface roughness of the material, SEM (scanning electron microscopy) analysis would be used.

Particle size analysis

The size of the particles, especially when lies in the range of nanodimensions, plays important role in modifying the properties of the materials. The particle size would also be determined for the XRD data using Scherrer's equation ($0.9\lambda/\beta\cos\theta$).

Film thickness

Aplha step D-Tencor T120 (surface profilometer) available at Dayalbagh Educational Institute, Agra will be used to measure film thickness.

Band gap

Using *Tauc* plots, Eg will be determined by plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$ using the equation 3.

$$\alpha = A\,(h\nu - Eg)^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

The absorption data will be recorded by using UV-Vis spectrophotometer (Shimadzu, UV-2450) in available in DEI.

Mott-Schottky plot

An LCR meter (available in the lab) would be employed to measure capacitance (C) at semiconductor electrolyte junction. $1/C^2$ versus electrode voltage plot will give flatband potential and donor/acceptor densities using the following the Mott-Schottky equation, the above parameters would be estimated.

$$\frac{1}{C^2} = \left(\frac{2}{q\varepsilon_o\varepsilon N_D}\right)\left(V_{app} - V_{FB} - \frac{kT}{q}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

Where ε_o is the permittivity of the vacuum, N_D is the donor density, V_{app} is the applied potential, ε is the dielectric constant of the semiconductor, kT/q is the temperature dependent term. Nature of semiconductor can be known from the slope as: positive Slope→ *n*- type; negative Slope→ *p*- type

5.2 Photo-electrochemical studies

Photo-electrochemical measurements would be done by employing semiconductor samples (thin films) as photosensitive working electrode, in conjunction with platinum counter electrode and saturated calomel electrode (SCE, as reference electrode), at varying electrolyte conditions. Nature and concentration of the electrolyte and electrolyte- pHs would be varied in order to optimize the conditions of H_2 evolution.

6. Expected out come

This research in the area of photoelectrochemical splitting of water for hydrogen generation not only filling the gap in the existing knowledge but would also help to optimize electrolytic parameters (pH, temperature and ionic strength) for efficient photoelectrochemical water splitting for hydrogen generation.

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